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ANHYDROUS CALCIUM DIOXIDE AND THE CONSTITUTION OF ITS HYDRATES

de Forcrand

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ABSTRACT: Anhydrous CaO_2 is dissolved in HCl to determine the heat of solution. The stability and heat of formation of CaO_2 and its hydrates are determined, and compared to analogous compounds of strontium and barium.

I. The hydrated precipitate of calcium dioxide $CaO_2 + 8H_2O$, which I investigated earlier, is capable of losing its crystallization water and of yielding anhydrous calcium dioxide. /1388*

To prevent it from giving up oxygen as a result of the heating effect, I had to desiccate it under a vacuum desiccator in the presence of phosphoric anhydride.

The hydrate used consisted of

$$CaO_{2.02} + 7.62\ H_2O$$

which came in pearl-shaped flakes. I prepared it by using 4 H_2O_2 in solution over CaO.

At the end of six days the dioxide formed an amorphous dry powder which upon analysis yielded the following:

Ca	54.45%
O as it pertains to CaO	21.78%
O in the dioxide state	20.45%
H_2O (balance)	3.32%

which yields the formula /1389

$$CaO_{1.94} + 0.13\ H_2O$$

or

$$0.94\ CaO_2 + 0.06\ CaO_2H_2 + 0.07\ H_2O$$

i.e. essentially anhydrous CaO_2.

*Numbers in the margin indicate pagination in the foreign text.

I did not push the dehydration any further since the dioxide had already lost its oxygen traces under cooling.

I dissolved this compound in a calculated amount of hydrochloric acid diluted for exact neutralization.

Taking into account the small amount of protoxide hydrate contained in it, I found

$$18.930 \text{ Cal for } CaO_2$$

Knowing the heat of solution of CaO in acid and the heat of formation of hydrogen peroxide, the following reaction can be calculated:

$$CaO \text{ (in sol.)} + O = CaO_2 \text{ (in sol.)} \ldots\ldots + 5.43 \text{ Cal.}$$

Earlier I had found

$$SrO \text{ (in sol.)} + O = SrO_2 \text{ (in sol.)} \ldots\ldots + 10.875$$

and Berthelot reported

$$BaO \text{ (in sol.)} + O = BaO_2 \text{ (in sol.)} \ldots\ldots + 12.10.$$

Thus, starting with anhydrous protoxide, the stability of the anhydrous dioxide increases as the atomic weight rises from calcium to barium. It is further known that barium dioxide alone can be obtained directly by passing free oxygen over BaO and furthermore under certain temperature limitations. Lime and strontium oxide cannot be dioxidized directly. This also explains why, particularly with calcium dioxide hydrates, one cannot obtain absolutely anhydrous dioxide, since during the last phase of the vacuum desiccation the hydrate loses some oxygen and the stability of the dioxide becomes comparable to that of hydrate. Moissan provided the value of the heat of formation of anhydrous lime (Ca + O = 145 Cal). Starting with the elements, we can make the following calculation:

$$Ca \text{ (in sol.)} + O_2 \text{ (gas)} = CaO_2 \text{ (in sol.)} \ldots\ldots\ldots +150.43 \text{ Cal,}$$

a number which is slightly higher than that resulting from

$$SrO_2 \text{ (+142.075 Cal)}$$

if the Thomsen data were to be observed: Sr + O = +131.2 Cal, which, however, /1390
is probably very close.

II. Let us now examine the two successive hydration states: CaO_2, $2H_2O$ and CaO_2, 8 or 9 H_2O, already described by Thenard and by Schoene. For the most hydrated compound we obtain the following:

CaO_2 (in sol.) + 8 H_2O (liq.)[1] = CaO_2, 8 H_2O (in sol.).... +15.636 Cal

CaO_2 (in sol.) + 8 H_2O (in sol.) = CaO_2, 8 H_2O (in sol.).... +4.196 Cal

i.e. for 1 H_2O (liq.) + 1.954 Cal and for 1 H_2O (in sol.).... +0.524 Cal

These numbers are very close to those which yield the two other dioxides [2].

However, if we calculate the transition from the first state to the second (2 H_2O to 8 H_2O), we find 6 H_2O (liq. fixed) + 17.851 Cal, i.e. +2.975 Cal for each molecule of water.

This number is higher than 1.954 Cal which is not tolerable. Consequently the fixation of the first two molecules of water on CaO_2 (in sol.) would absorb -2.215 Cal while the six latter molecules would release +15.636 Cal.

This conclusion must be discarded and the conclusion should be drawn that the first compound CaO_2, 2 H_2O is not a real dioxide hydrate, but a combination of hydrogen peroxide and lime hydrate

$$CaO_2H_2 + H_2O_2,$$

which explains its varying properties.

The heat of formation of this compound can even be calculated with the data which I published

CaO_2H_2 (in sol.) + H_2O_2 (diss.) = CaO_2H_2, H_2O_2 (in sol.).... +9.815 Cal.

I have explained earlier that this particular compound is produced between +10° and +16° if hydrogen peroxide is added to lime in solution without exceeding the 2 H_2O_2 amount, or by exceeding it while increasing the temperature to 20° so that the only true hydrate with 8 H_2O is formed only with 3 or 4 molecules of hydrogen peroxide and at low temperature.

This leads to a supplementary release of heat of +17.851 Cal, but this does not correspond to a simple addition of 6 molecules of water; actually, the work produced now is the following: /1391

Absorption

	Cal
Destruction of the compound CaO_2H_2, H_2O_2	- 9.815
Dehydration of CaO_2H_2	- 15.100
Total	- 24.915

[1] I am assuming here preferably $8H_2O$ since analyses sometimes gave me more sometimes less than $8H_2O$.

[2] SrO yielded +2.275 Cal for 1 H_2O (liq.) and BaO + 1.82 Cal (Comptes rendus, Vol. 130, p. 1,019).

Realease

	Cal
Destruction of H_2O_2 (diss.)	+ 21.7
Combination of oxygen with CaO (in sol.)	+ 5.43
Hydration of CaO_2 (in sol.)	+ 15.636
Total	+ 42.766

Finally, this means +42.766 Cal - 24.915 Cal = +17.851 Cal of which only +15.636 Cal represents the amount of heat released for the hydration per 8 molecules of water, corresponding to a rather unstable hydrate.

The strontium and barium dioxides do not exhibit any complexity of this type.

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